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Supporting Information

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Iridium-Catalyzed Enantioselective Synthesis of Allylic Alcohols Using Silanolates as Hydroxide Equivalents

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All reactions were performed in oven dried glass ware under argon. For the reactions, solvents were purified by distillation and dried by passage over activated alumina under an argon atmosphere (H_2O content < 30 ppm, *Karl-Fischer* titration). All allylic carbonates were prepared by the reaction of the corresponding allylic alcohol with di-*tert*-butyl carbonate catalyzed by $Bu_4N{\bullet}HSO_4$ as phase transfer reagents.[1] Commercially available chemicals were used as received unless noted otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN Mercury 300 MHz or a Gemini 300 MHz. Infrared spectra were recorded on a Perkin-Elmer spectrum RX-I FT-IR. High resolution mass spectra were obtained on a VG-TRIBRID for electron impact

ionization (EI) or on a TSQ 7000 for electron-spray ionization (ESI). Enantiomeric excesses were determined by chiral HPLC analysis with Merck-Hitachi D-7000 system and Daicel columns, or by chiral GC analysis on a Hewlett-Packard HP 6890 series apparatus. Optical rotation $[a]_D$ were measured on a Jasco DIP-1000 Polarimeter. The absolute configurations were assigned by comparison of the $[a]_D$ values of known compounds. For the new adducts, it was assigned based on the established stereochemical outcome of the reaction.

Synthesis of potassium silanolates:

A solution of trialkylsilanol (5 mmol, 1 equiv) in Et_2O (5 mL) was added dropwise to a suspension of KH (7.5 mmol, 1.5 equiv) in Et_2O (10 mL) at RT. The reaction mixture was stirred for 1 h, then filtered through cotton wool and concentrated in vacuo. Potassium silanolates could be stored under argon in a refrigerator for prolonged period of time.

General Procedure 1, for the reaction between *tert*-butylcarbonates and potassium silanolates and subsequent silyl ether cleavage:

A Schlenk under argon was charged with $[Ir(cod)Cl]_2$ (10.1 mg, 15 μmol, 3 mol%) and (*S*)-(+)-(3,5-Dioxa-4-phopshacyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)bis[(1*S*)-1-phenylethyl]amine (16.2 mg, 30 μmol, 6 mol%). THF (0.5 mL) and *n*-propylamine (0.5 mL) were added, and the reaction mixture was stirred at 50 °C for 30 min. The solution was allowed to cool to RT, and the volatiles were removed under high vacuum (30 min). A solution of potassium silanolate (1.00 mmol, 2 equiv) in CH_2Cl_2 (2 mL) was added, followed by *tert*-butyl carbonate (0.50 mmol, 1 equiv) in CH_2Cl_2 (2 mL), and the reaction mixture was stirred at RT. After the reaction was complete (usually 14 h), as determined by TLC, the crude mixture was partitioned between H_2O (20 mL) and CH_2Cl_2 (20 mL). The aqueous layer was re-extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude silyl ether. The ratio of regioisomers was determined by ^1H NMR analysis of the crude sample.

General Procedure 1a: Silyl ether cleavage using TBAF in THF

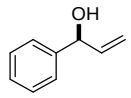
The crude mixture was taken up in THF (5 mL), cooled to 0 °C, and treated with TBAF (1 M in THF, 1 mL, 2 equiv). The reaction mixture was stirred for 2 h, then partitioned between H_2O (50 mL) and CH_2Cl_2 (20 mL). The aqueous layer was re-extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic alcohol. Purification by flash column chromatography (10% Et_2O in hexanes or pentane) afforded the desired product. Some allylic alcohols are volatile.

General Procedure 1b: Silyl ether cleavage using 30% aq. NaOH in methanol

The crude mixture was taken up in methanol (3 mL), cooled to 0 °C, and treated with 0.3 mL 30% aqueous sodium hydroxide. The reaction mixture was stirred for 4 h, then partitioned between H_2O (50 mL) and Et_2O (20 mL). The aqueous layer was re-extracted with Et_2O (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude allylic alcohol. Purification by flash column chromatography (10% Et_2O in

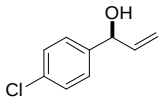
hexanes or pentane) afforded the desired product. Some allylic alcohols are volatile.

(*S*)-1-phenylprop-2-en-1-ol (Table 2, entry 1)



Following the general procedures 1 and 1b using *tert*-butyl cinnamyl carbonate and potassium triethylsilanolate (Table 2, entry 1), the desired product was isolated as a colorless oil (59 mg, 88%). The enantioselectivity was 97% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(major)}$ = 26.3 min, $t_{r(minor)}$ = 33.1 min). $[\alpha]_D^{25}$ -5.9 (*c* 1.73, PhH), Lit.[2] $[\alpha]_D^{25}$ -9.90 (*c* 5.14, PhH). ^{1}H NMR (300 MHz, $CDCl_3$) δ. All other spectroscopic data was in agreement with the literature.[2]

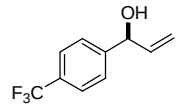
(*S*)-1-(4-chlorophenyl)prop-2-en-1-ol (Table 2, entry 2)



Following the general procedures 1 and 1b using (*E*)-*tert*-butyl 3-(4-chlorophenyl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 2), the desired product was isolated as a colorless oil (62.4 mg, 74%). The enantioselectivity was 98% ee (OJ-H, 220 nm, hexane:2-

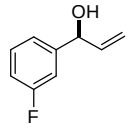
propanol = 95:5, flow rate 1 ml/min, $t_{r(major)}$ = 12.3 min, $t_{r(minor)}$ = 13.6 min). $[\alpha]_D^{26}$ +15.3 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 4H), 6.15-5.92 (m, 1H), 5.34 (d, J = 17.1 Hz, 1H), 5.23-5.16 (m, 2H), 2.05 (br s, 1H). All other spectroscopic data was in agreement with the literature.[3]

(*S*)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (Table 2, entry 3)



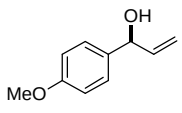
Following the general procedures 1 and 1b using (*E*)-*tert*-butyl 3-(4-(trifluoromethyl)phenyl)allyl carbonate and potassium triethylsilanolate (Table 2, entry 3), the desired product was isolated as a colorless oil (78.8 mg, 78%). The enantioselectivity was 98% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(major)}$ = 16.5 min, $t_{r(minor)}$ = 18.3 min). $[\alpha]_D^{35}$ +11.7 (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.63-7.58 (m, 2H), 7.50-7.45 (m, 2H), 6.06-5.92 (m, 1H), 5.36 (d, J = 17.1 Hz, 1H), 5.27-5.20 (m, 2H), 2.29 (br s, 1H). All other spectroscopic data was in agreement with the literature.[3]

(*S*)-1-(3-fluorophenyl)prop-2-en-1-ol (Table 2, entry 4)



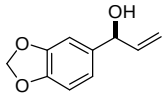
Following the general procedures 1 and 1a using (*E*)-*tert*-butyl 3-(3-fluorophenyl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 4), the desired product was isolated as a colorless oil (48.7 mg, 64%). The enantioselectivity was 98% ee (GC, Supelco β-dex 120, 95 °C isotherm, 2 mL H_2 / min, split ratio 40:1, $t_{r(minor)}$ = 29.6 min, $t_{r(major)}$ = 30.5 min). $[\alpha]_D^{35}$ +12.1 (*c* 0.56, $CHCl_3$); IR (thin film) ν 3339, 1615, 1590, 1448, 1247, 928, 631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.25 (m, 1H), 7.12-7.03 (m, 1H), 7.00-6.91 (m, 1H), 6.03-5.90 (m, 1H), 5.31 (d, J = 17.1 Hz, 1H), 5.19 (d, J = 10.3 Hz, 1H), 5.15-5.10 (m, 1H), 2.88 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7 (d, J = 245.2 Hz), 144.9 (d, J = 6.9 Hz), 139.5, 129.8 (d, J = 8.1 Hz), 121.7 (d, J = 2.6 Hz), 115.6, 114.3 (d, J= 21.1 Hz), 113.1 (d, J = 22.1 Hz), 74.6; HR-EI-MS *m/z* calcd for C_9H_8FO $[M-H]^+$ 151.0554, found 151.0557.

(*S*)-1-(4-methoxyphenyl)prop-2-en-1-ol (Table 2, entry 5)



Following the general procedures 1 and 1b using (*E*)-*tert*-butyl 3-(4-(methoxy)phenyl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 5), the desired product was isolated as a colorless oil (61.6 mg, 75%). The enantioselectivity was 95% ee (OD-H, 220 nm, hexane:2-propanol = 90:10, flow rate 0.7 ml/min, $t_{r(minor)}$ = 10.9 min, $t_{r(major)}$ = 12.5 min). $[\alpha]_D^{26}$ -6.04 (*c* 1.0, $CHCl_3$), Lit.[4] $[\alpha]_D^{25}$ +4.2 (*c* 1.11, $CHCl_3$) for (*R*) enantiomer; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 6.91-6.87 (m, 2H), 6.11-5.98 (m, 1H), 5.34 (d, J = 17.1 Hz, 1H), 5.21-5.15 (m, 2H), 3.80 (s, 3H), 1.91 (br s, 1H). All other spectroscopic data was in agreement with the literature.[4]

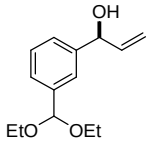
(*S*)-1-(benzo[d][1,3]dioxol-5-yl)prop-2-en-1-ol (Table 2, entry 6)



Following the general procedures 1 and 1b using (*E*)-3-(benzo[d][1,3]dioxol-5-yl)allyl *tert*-butyl carbonate and potassium triethylsilanolate (Table 2, entry 6), the desired product was isolated as a colorless oil (64.1 mg, 72%). The enantioselectivity was 92% ee (OD-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(minor)}$ = 27.5 min, $t_{r(major)}$ = 34.0 min). $[\alpha]_D^{35}$ +1.01 (*c* 0.5, $CHCl_3$); ^{1}H NMR

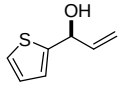
(300 MHz, $CDCl_3$) δ 6.88-6.75 (m, 3H), 6.07-5.95 (m, 1H), 5.94 (s, 2H), 5.34 (dd, J = 17.1, 1.4 Hz, 1H), 5.19 (dd, J = 10.3, 1.3 Hz, 1H), 1.93 (br s, 1H). All other spectroscopic data was in agreement with the literature.[5]

(*S*)-1-(3-(diethoxymethyl)phenyl)prop-2-en-1-ol (Table 2, entry 7)



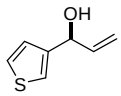
Following the general procedures 1 and 1a using (*E*)-*tert*-butyl 3-(3-(diethoxymethyl)phenyl)allyl carbonate and potassium triethylsilanolate (Table 2, entry 7), the desired product was isolated as a colorless oil (82.7 mg, 70%). The enantioselectivity was 98% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(major)}$ = 15.9 min, $t_{r(minor)}$ = 21.4 min). $[\alpha]_D^{35}$ -0.46 (*c* 1, $CHCl_3$); IR (thin film) ν 3408, 2976, 2879, 1334, 1050, 910, 631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.26 (m, 4H), 6.02-5.96 (m, 1H), 5.42 (s, 1H), 5.26 (d, J = 17.1 Hz, 1H), 5.13-5.08 (m, 2H), 3.58-3.43 (m, 4H), 2.65 (br s, 1H), 1.17 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 140.1, 139.1, 128.3, 126.2, 125.8, 124.6, 114.9, 101.4, 75.1, 61.1, 15.3; HR-EI-MS *m/z* calcd for $C_{12}H_{15}O_2$ $[M\text{-}OEt]^+$ 191.1067 found 191.1068.

(*S*)-1-(thiophen-2-yl)prop-2-en-1-ol (Table 2, entry 8)



Following the general procedures 1 and 1b using (*E*)-*tert*-butyl 3-(thiophen-2-yl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 8), the desired product was isolated as a slightly yellow oil (43.5 mg, 62%). The enantioselectivity was 99% ee (OD-H, 220 nm, hexane:2-propanol = 99:1, flow rate 1 ml/min, $t_{r(minor)}$ = 27.1 min, $t_{r(major)}$ = 29.0 min). $[\alpha]_D^{26}$ +18.4 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.26 (m, 1H), 7.02-6.96 (m, 2H), 6.19-6.06 (m, 1H), 5.45-5.35 (m, 2H), 5.26 (d, J = 10.3 Hz, 1H), 2.19 (br s, 1H). All other spectroscopic data was in agreement with the literature.[6]

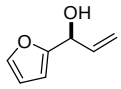
(*S*)-1-(thiophen-3-yl)prop-2-en-1-ol (Table 2, entry 9)



Following the general procedures 1 and 1a using (*E*)-*tert*-butyl 3-(thiophen-3-yl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 9), the desired product was isolated as a slightly yellow oil (47.0 mg, 67%). The enantioselectivity was 98% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(minor)}$ = 27.5 min,

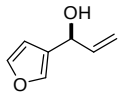
$t_{r(major)}$ = 36.9 min). $[\alpha]_D^{35}$ +13.4 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.26 (m, 1H), 7.20-7.15 (m, 1H), 7.04 (dd, J = 5.0, 1.0 Hz, 1H), 6.09-5.96 (m, 1H), 5.30 (dd, J = 17.1, 1.0 Hz, 1H), 5.20-5.15 (m, 2H), 3.23 (br s, 1H). All other spectroscopic data was in agreement with the literature.[6]

(*S*)-1-(furan-2-yl)prop-2-en-1-ol (Table 2, entry 10)



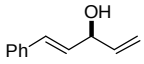
Following the general procedures 1 and 1a using (*E*)-*tert*-butyl 3-(furan-2-yl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 10), the desired product was isolated as a slightly orange oil (31.0 mg, 50%). The enantioselectivity was 97% ee (OJ-H, 220 nm, hexane:2-propanol = 95:5, flow rate 1 ml/min, $t_{r(major)}$ = 12.9 min, $t_{r(minor)}$ = 14.6 min). $[\alpha]_D^{26}$ +1.14 (*c* 0.5, $CHCl_3$), Lit.[7] $[\alpha]_D^{25}$ -1.74 (*c* 2.41, $CHCl_3$) for (R) enantiomer; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 6.33 (s, 1H), 6.26 (s, 1H), 6.19-6.06 (m, 1H), 5.43 (d, J = 17.2 Hz, 1H), 5.32-5.21 (m, 2H), 2.12 (d, J = 4.3 Hz, 1H). All other spectroscopic data was in agreement with the literature.[7]

(*S*)-1-(furan-3-yl)prop-2-en-1-ol (Table 2, entry 11)



Following the general procedures 1 and 1a using (*E*)-*tert*-butyl 3-(furan-3-yl)allyl carbonate and potassium triethyl silanolate (Table 2, entry 11), the desired product was isolated as a colorless oil (37.2 mg, 60%). The enantioselectivity was 99% ee (OJ-H, 220 nm, hexane:2-propanol = 95:5, flow rate 1 ml/min, $t_{r(major)}$ = 11.6 min, $t_{r(minor)}$ = 12.9 min). $[\alpha]_D^{26}$ 9.2 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 2H), 6.40 (s, 1H), 6.12-5.99 (m, 1H), 5.35 (d, J = 17.1 Hz, 1H), 5.23-5.10 (m, 2H), 2.01 (d, J = 4.6 Hz, 1H). All other spectroscopic data was in agreement with the literature.[6]

(*S,E*)-1-phenylpenta-1,4-dien-3-ol (Table 2, entry 12)



Following the general procedures 1 and 1a using *tert*-butyl (2*E*,4*E*)-5-phenylpenta-2,4-dienyl carbonate and potassium triethyl silanolate (Table 2, entry 12), the desired product was isolated as a colorless oil (52.1 mg, 65%). The enantioselectivity was 97% ee (OJ-H, 220 nm, hexane:2-propanol = 93:7, flow rate 0.8 ml/min, $t_{r(major)}$ = 15.5 min,

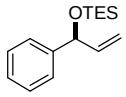
$t_{r(minor)}$ = 20.3 min). $[\alpha]_D^{35}$ 34.1 (*c* 0.3, $CHCl_3$), Lit.[8] $[\alpha]_D^{25}$ +38.5 (*c* 1.9, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.16 (m, 5H), 6.62 (dd, J = 15.9, 0.9 Hz, 1H), 6.25 (dd, J = 15.9, 6.4 Hz, 1H), 6.05-5.92 (m, 1H), 5.35 (dt, J = 17.2, 1.4 Hz, 1H), 5.21 (dt, J = 10.4, 1.3 Hz, 1H), 4.85-4.77 (m, 1H). All other spectroscopic data was in agreement with the literature.[8]

General Procedure 2, for the synthesis of silyl ethers:

A Schlenk under argon was charged with $[Ir(cod)Cl]_2$ (20.2 mg, 30 μmol, 3 mol%) and (*S*)-(+)-(3,5-Dioxa-4-phopshacyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)bis[(1*S*)-1-phenylethyl]amine (32.4 mg, 60 μmol, 6 mol%). THF (0.7 mL) and *n*-propylamine (0.7 mL) were added, and the reaction mixture was stirred at 50 °C for 30 min. The solution was allowed to cool to RT, and the volatiles were removed under high vacuum (30 min). A solution of potassium silanolate (1.00 mmol, 2 equiv) in CH_2Cl_2 (2 mL) was added, followed by *tert*-butyl carbonate (0.50 mmol, 1 equiv) in CH_2Cl_2 (2 mL), and the reaction mixture was stirred at RT for 1 to 2 days. The crude mixture was partitioned between H_2O (20 mL) and Et_2O (20 mL). The aqueous layer was re-extracted with Et_2O (3 × 15 mL). The combined organic layers were dried (Na_2SO_4)

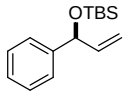
and concentrated under reduced pressure to afford the crude silyl ether, which was purified by flash column chromatography (1% Et_2O in pentane).

(*S*)-triethyl(1-phenylallyloxy)silane (Table 1, entry 5)



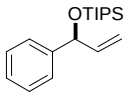
Following the general procedure 2 using *tert*-butyl cinnamyl carbonate and potassium triethylsilanolate (Table 1, entry 5), the desired product was isolated as a colorless oil (100.2 mg, 81%). The enantioselectivity was established after silyl ether cleavage (see previously): 97% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(major)}$ = 26.3 min, $t_{r(minor)}$ = 33.1 min). $[\alpha]_D^{25}$ -31.2 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 6.00-5.88 (m, 1H), 5.28 (d, J = 17.0 Hz, 1H), 5.16 (d, J = 5.9 Hz, 1H), 5.08 (d, J = 10.1 Hz, 1H), 0.95-0.89 (m, 9H), 0.65-0.57 (m, 6H). All other spectroscopic data was in agreement with the literature.[9]

(*S*)-*tert*-butyldimethyl(1-phenylallyloxy)silane (Table 1, entry 7)



Following the general procedure 2 using *tert*-butyl cinnamyl carbonate and potassium tert-butyldimethylsilanolate (Table 1, entry 7), the desired product was isolated as a colorless oil (98.1 mg, 79%). The enantioselectivity was established after silyl ether cleavage (see previously): 98% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(major)}$ = 26.3 min, $t_{r(minor)}$ = 33.1 min). $[\alpha]_D^{25}$ -34.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 6.00-5.87 (m, 1H), 5.30 (d, J = 17.0 Hz, 1H), 5.18 (d, J = 5.7 Hz, 1H), 5.08 (d, J = 10.2 Hz, 1H), 0.94 (s, 9H), 0.10 (s, 3H), 0.02 (s, 3H). All other spectroscopic data was in agreement with the literature.[10]

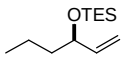
(*S*)-triisopropyl(1-phenylallyloxy)silane (Table 1, entry 8)



Following the general procedure 2 using *tert*-butyl cinnamyl carbonate and potassium triisopropylsilanolate (Table 1, entry 8), the desired product was isolated as a colorless oil (92.9 mg, 64%). The enantioselectivity was established

after silyl ether cleavage (see previously): 99% ee (OJ-H, 220 nm, hexane:2-propanol = 98:2, flow rate 1 ml/min, $t_{r(major)}$ = 26.3 min, $t_{r(minor)}$ = 33.1 min). $[\alpha]_D^{25}$ -32.0 (*c* 0.5, $CHCl_3$); IR (thin film) ν 2943, 2866, 1463, 1129, 1062, 882, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.24 (m, 5H), 6.00-5.88 (m, 1H), 5.32-5.25 (m, 2H), 5.07-5.03 (m, 1H), 1.07-0.99 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 142.2, 128.1, 127.0, 126.0, 112.8, 76.1, 18.0, 12.3; Combustion Analysis: Anal. calcd for $C_{18}H_{30}OSi$: C, 74.42; H, 10.41; found C, 74.21; H, 10.52.

(*R*)-(hex-1-en-3-yloxy)triethylsilane (Table 2, entry 13)



A Schlenk under argon was charged with $[Ir(cod)Cl]_2$ (20.2 mg, 30 μmol, 3 mol%) and (*S, S, S*)-**L** (32.4 mg, 60 μmol, 6 mol%). THF (0.7 mL) and *n*-propylamine (0.7 mL) were added, and the reaction mixture was stirred at 50 °C for 30 min. The solution was allowed to cool to RT, and the volatiles were removed under high vacuum (30 min). A solution of potassium triethylsilanolate (340 mg, 2.00 mmol, 2 equiv) in THF (2 mL) was added, followed by (*E*)-*tert*-butyl hex-2-enyl carbonate (200.3 mg, 1.00 mmol, 1 equiv) in THF (2 mL), and the reaction mixture was stirred at RT for 2 days.

The crude mixture was partitioned between H_2O (20 mL) and Et_2O (20 mL). The aqueous layer was re-extracted with Et_2O (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude silyl ether. Purification by flash column chromatography (1% Et_2O in pentane) afforded the desired product as a colorless oil (139.4 mg, 65%). $[\alpha]_D^{26}$ -4.6 (*c* 2.0, $CHCl_3$); IR (thin film) ν 2957, 2877, 1459, 1097, 1005, 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.86-5.73 (m, 1H), 5.13 (d, J = 17.1 Hz, 1H), 5.01 (dd, J = 10.3, 1.0 Hz, 1H), 4.10-4.01 (m, 1H), 1.60-1.29 (m, 4H), 0.98-0.89 (m, 12H), 0.64-0.53 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 113.4, 73.7, 40.5, 18.6, 14.2, 7.0, 5.1; Combustion Analysis: Anal. calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22; found C, 67.08; H, 11.96.

To measure the ee of the product, it was converted to the corresponding benzoyl ester[11] by cleavage of the TES ether and treatment with benzoyl chloride, using the same procedure as for compound of entry 13. ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.50 (m, 3H), 5.90 (m, 1H), 5.53 (m, 1H), 5.28 (m, 2H), 1.75 (m, 2H), 1.45 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). HPLC analysis indicated that the enantiomeric excess of the ester was 95% (OB, 220 nm, hexane, flow rate 0.8 ml/min, $t_{r(minor)}$ = 9.40 min, $t_{r(major)}$ = 11.8 min).

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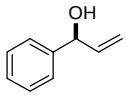
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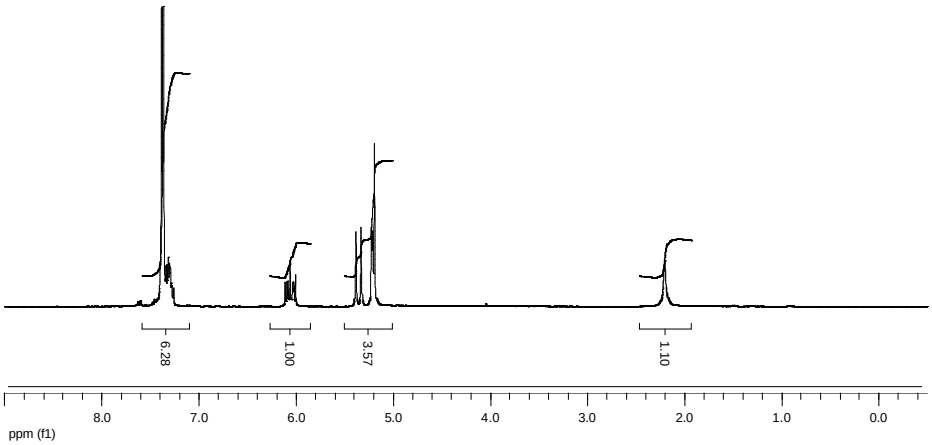
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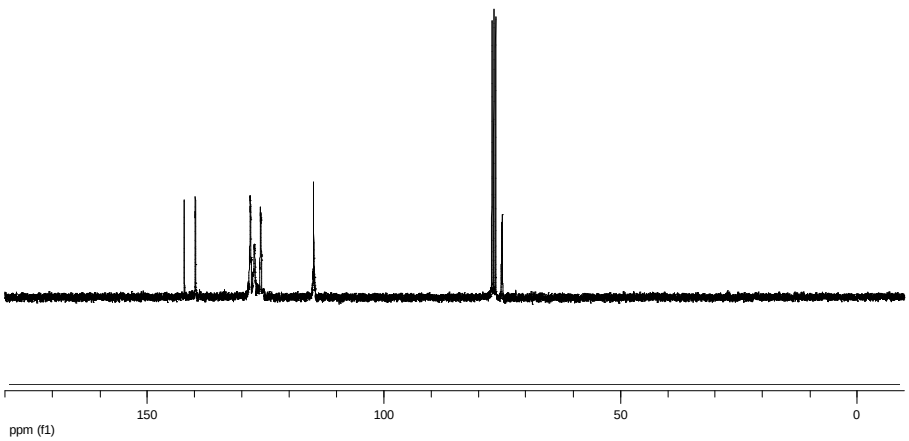
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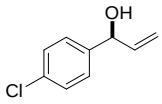
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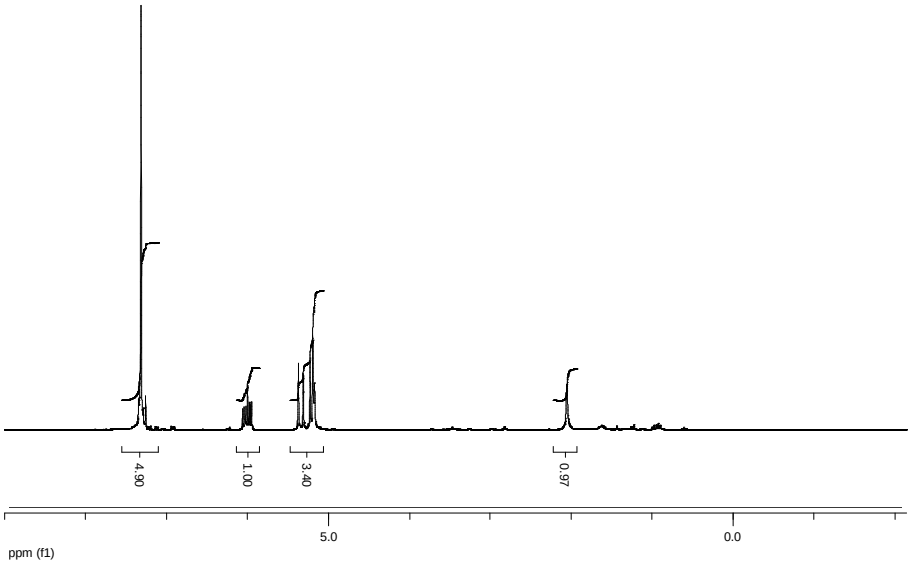
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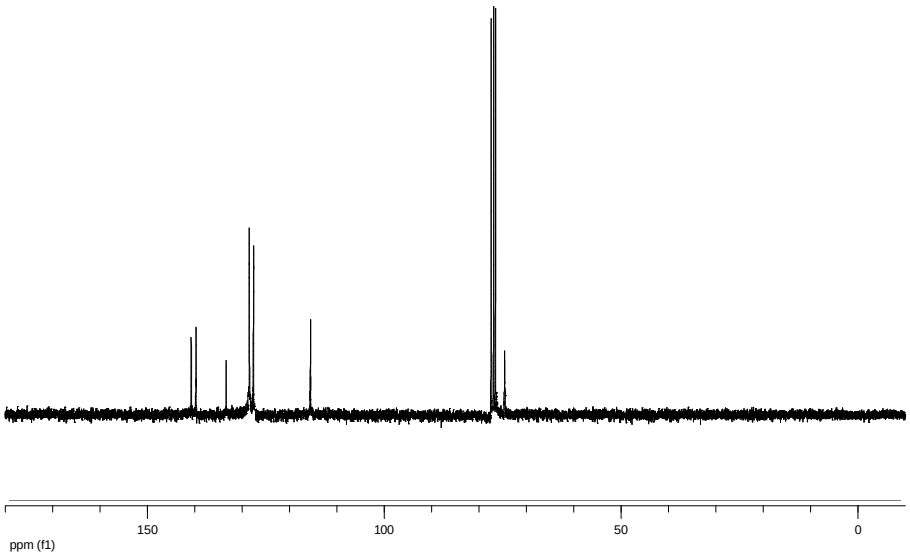
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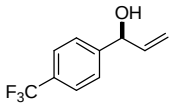
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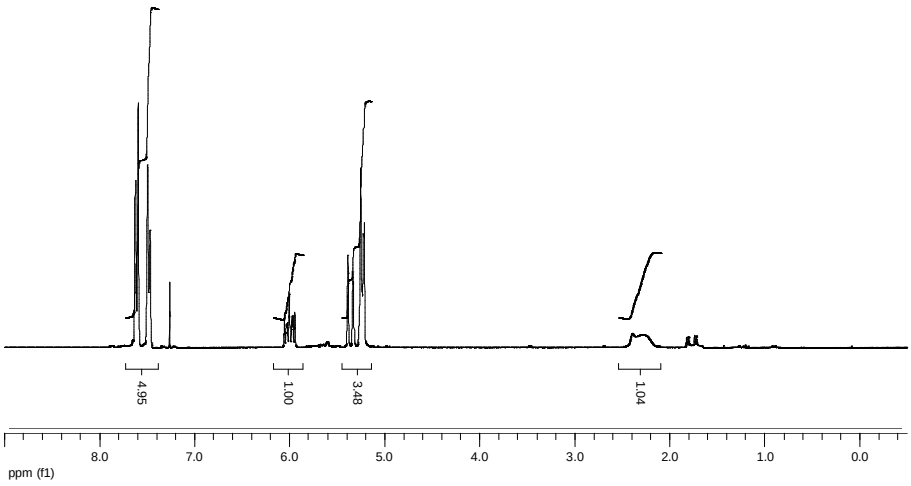
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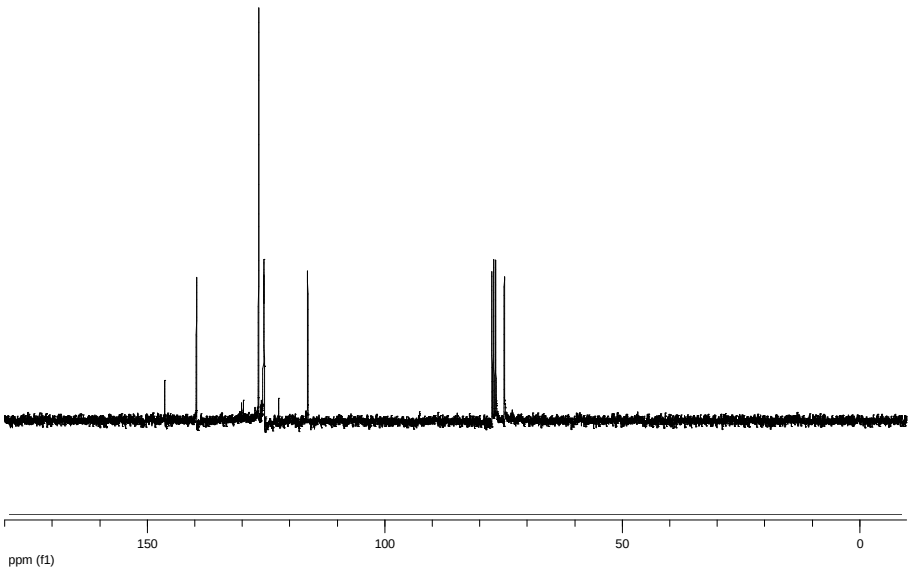
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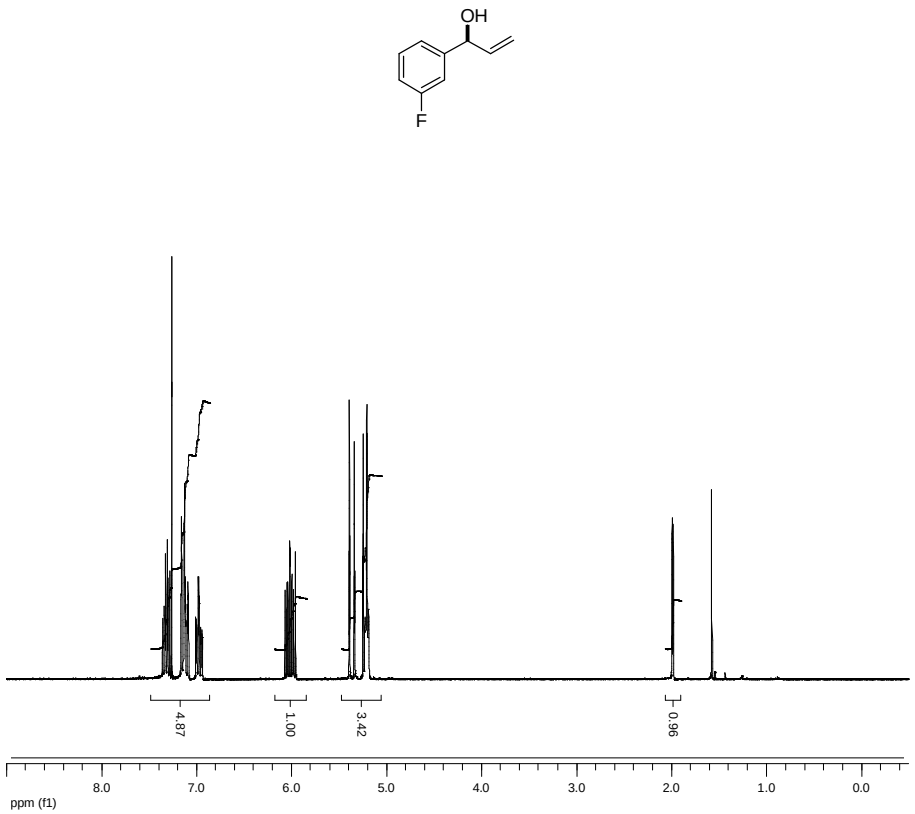
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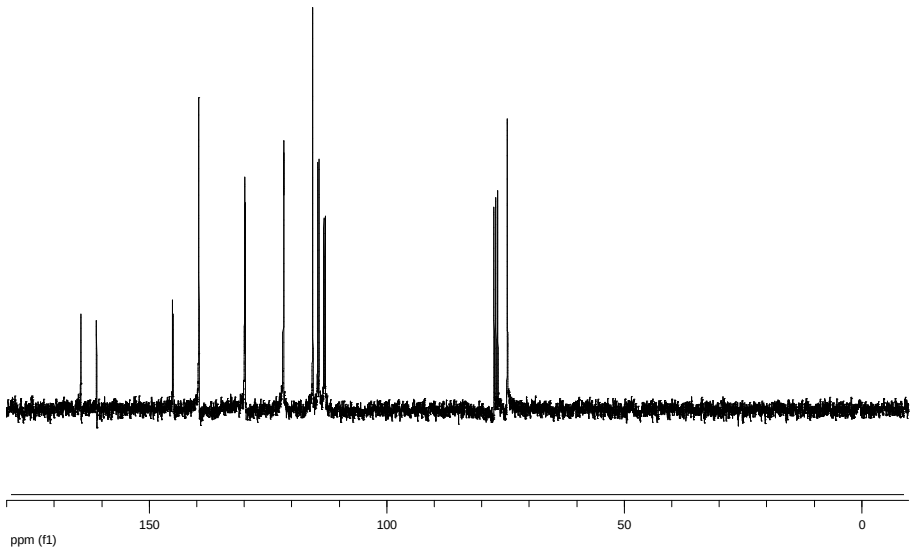
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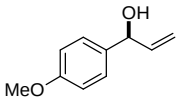
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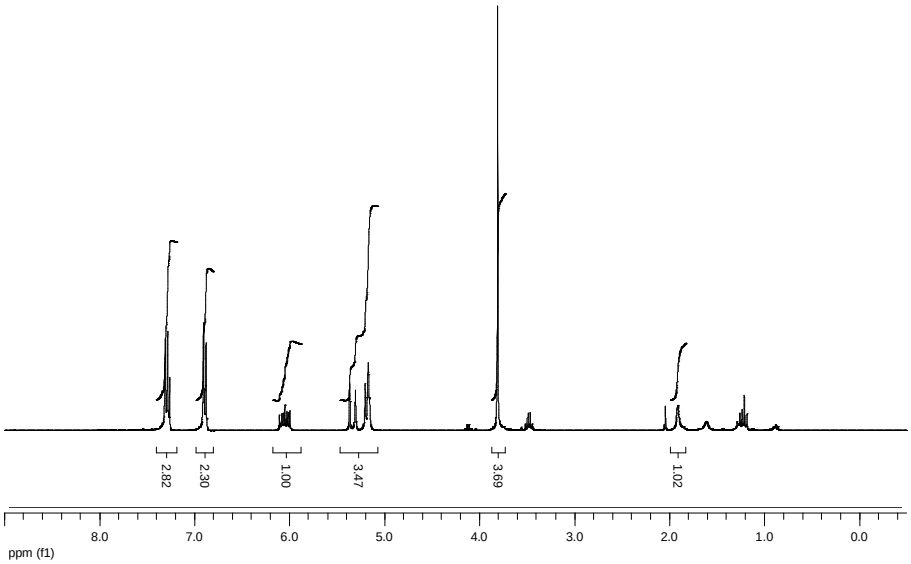
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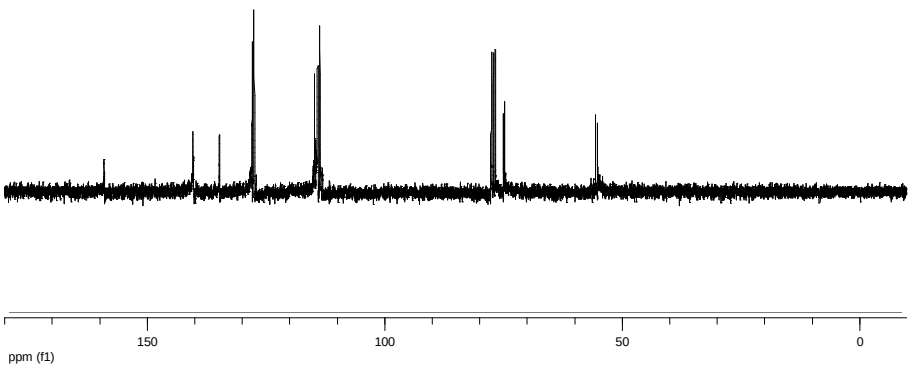
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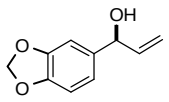
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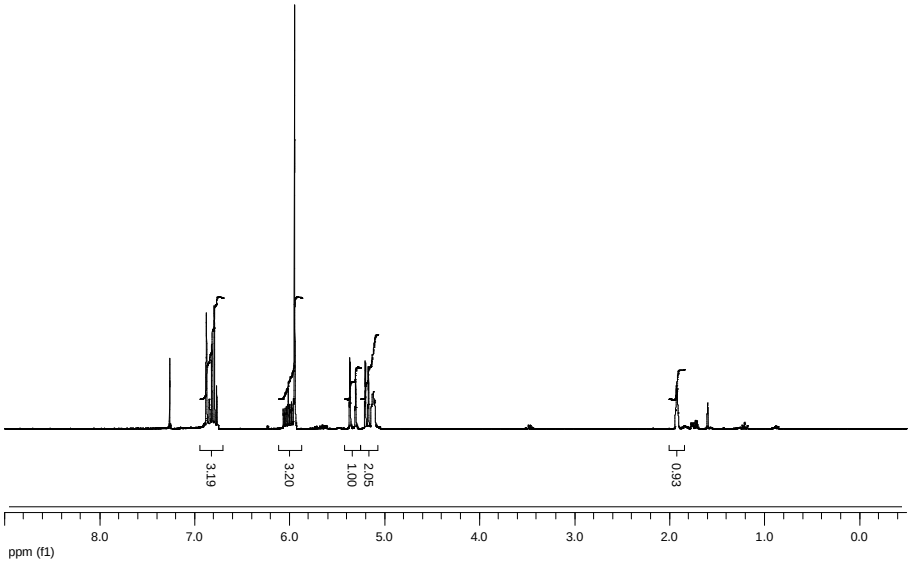
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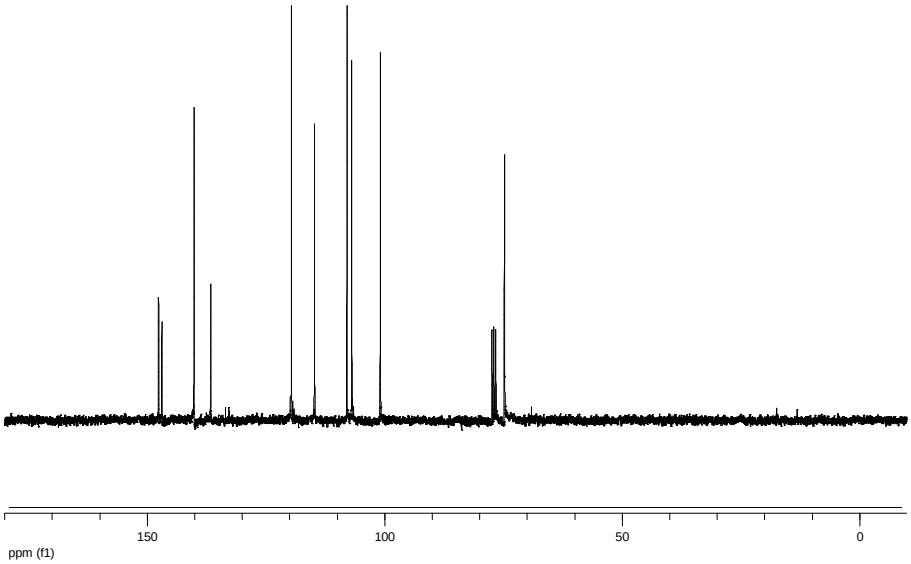
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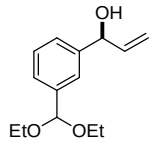
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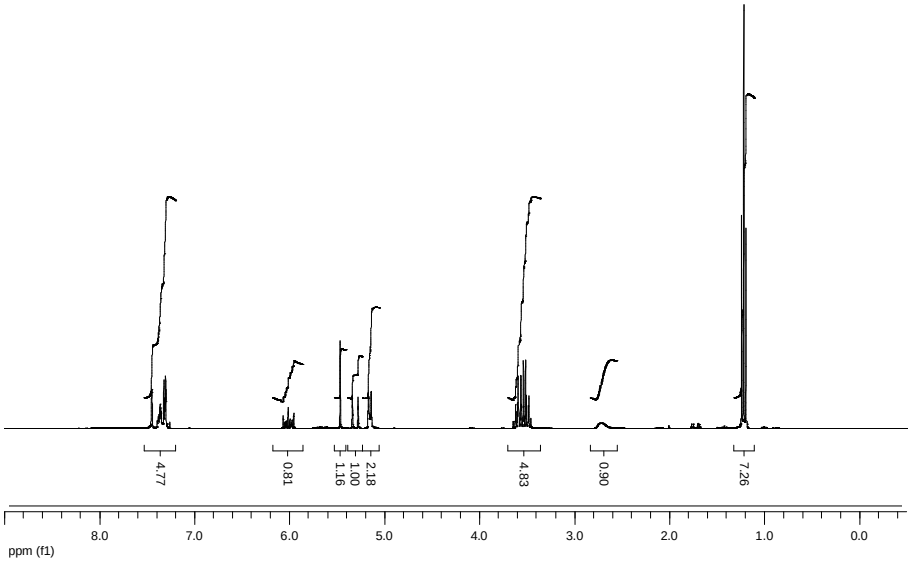
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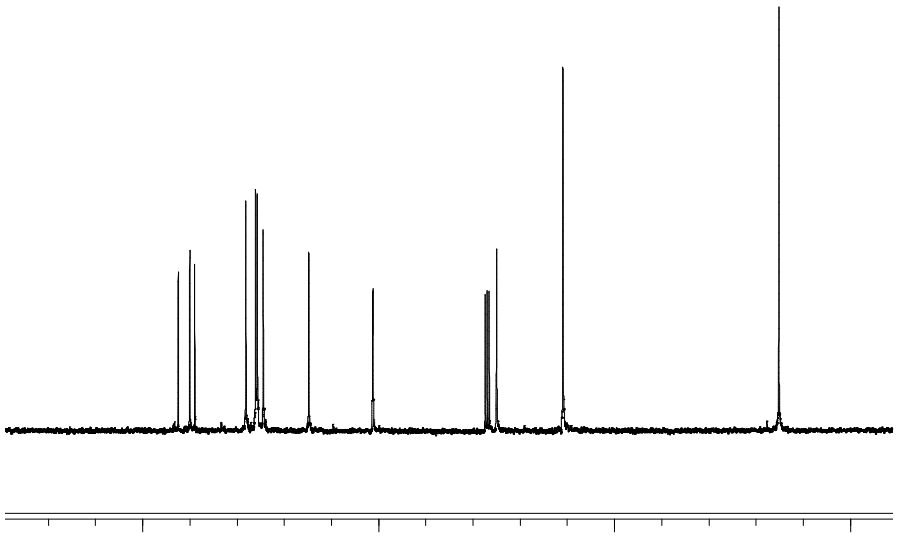

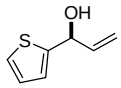
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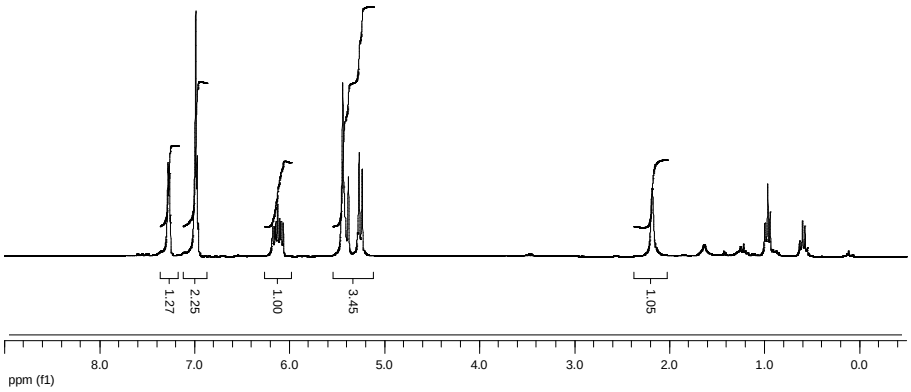
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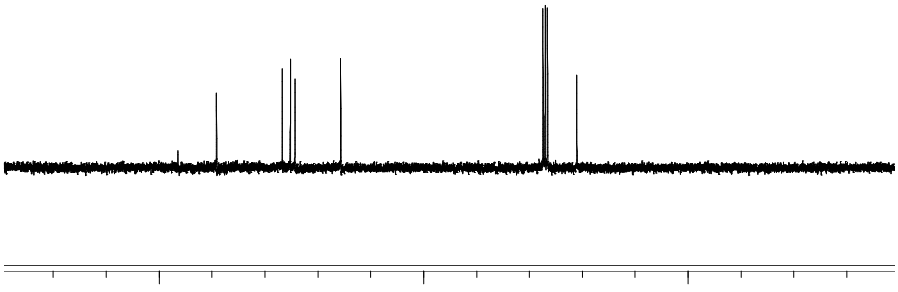

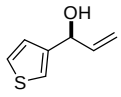
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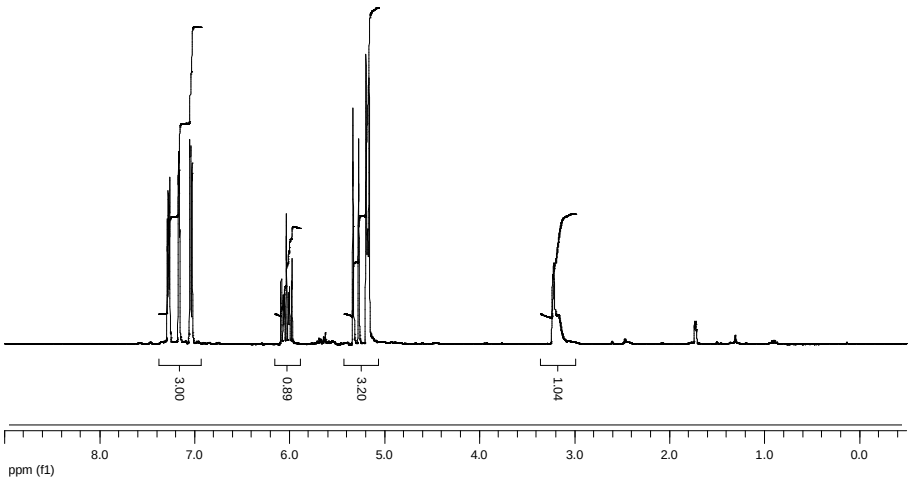
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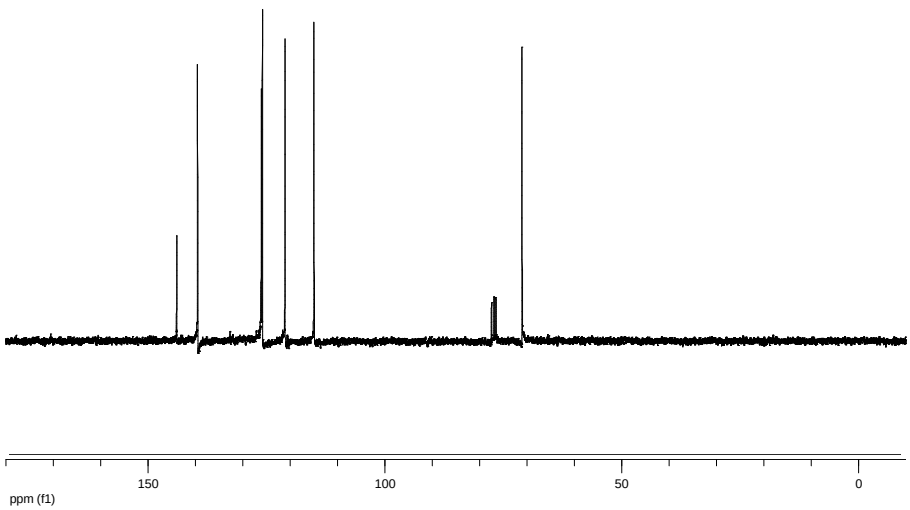
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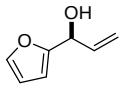
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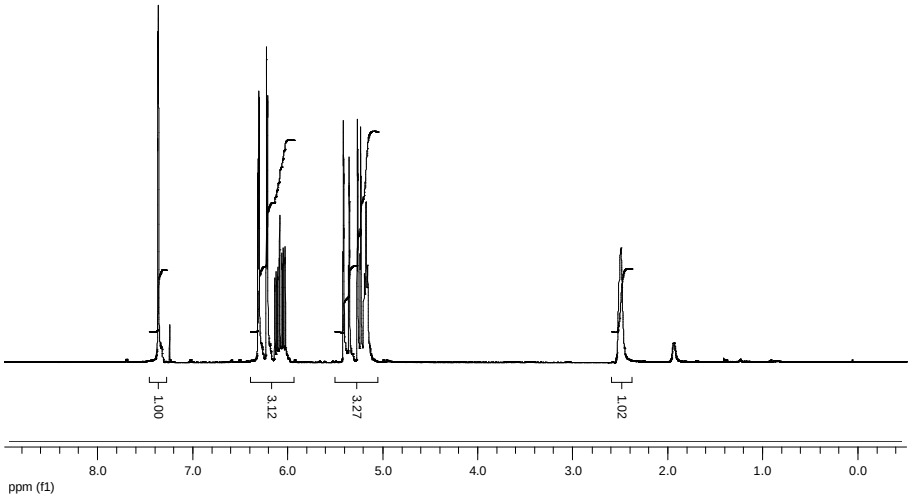
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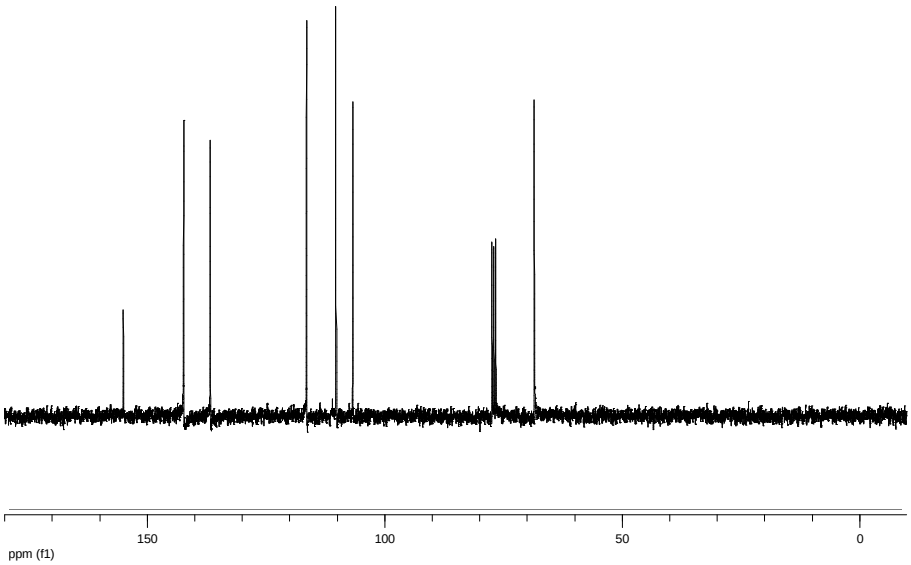
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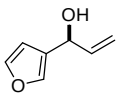
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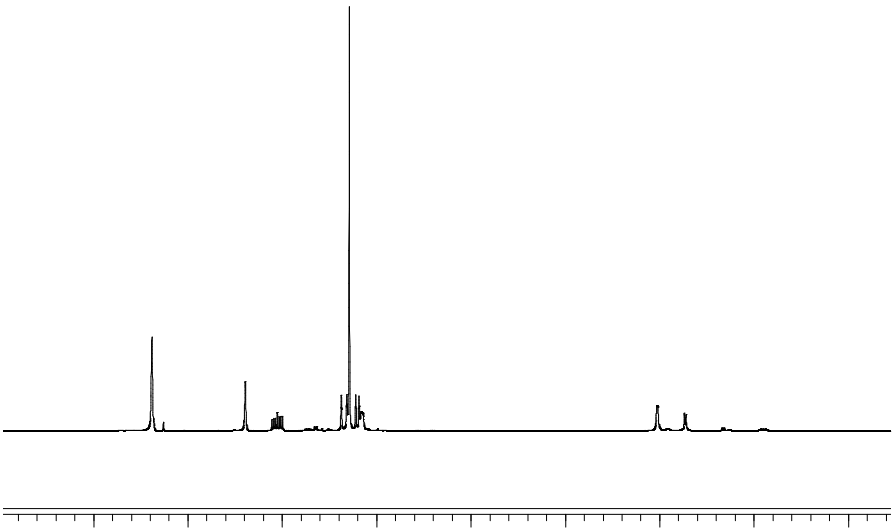

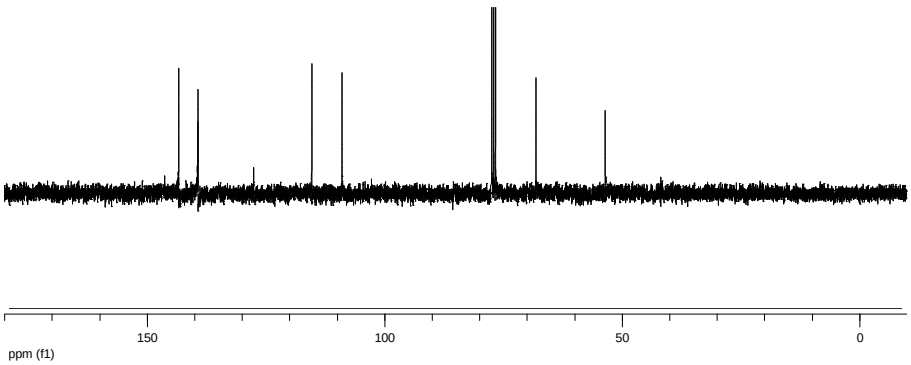
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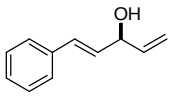
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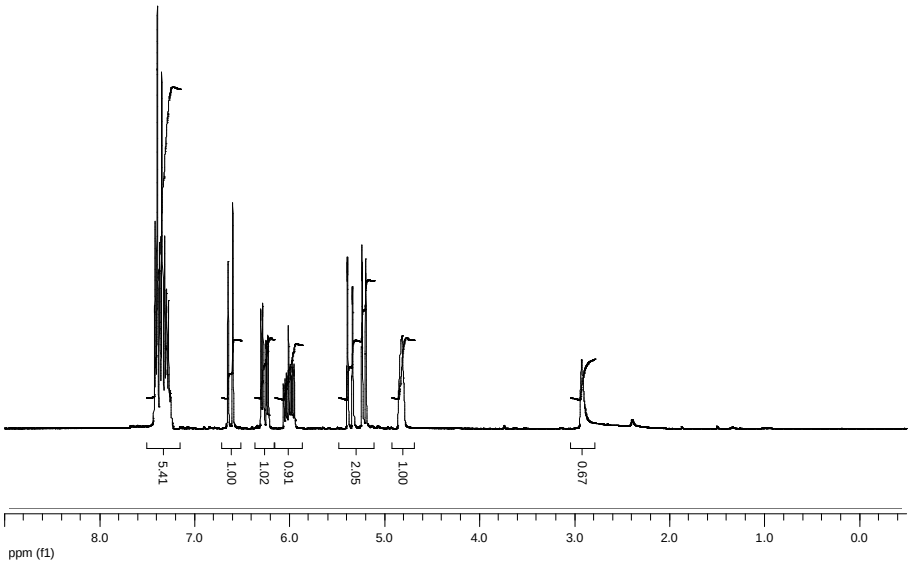
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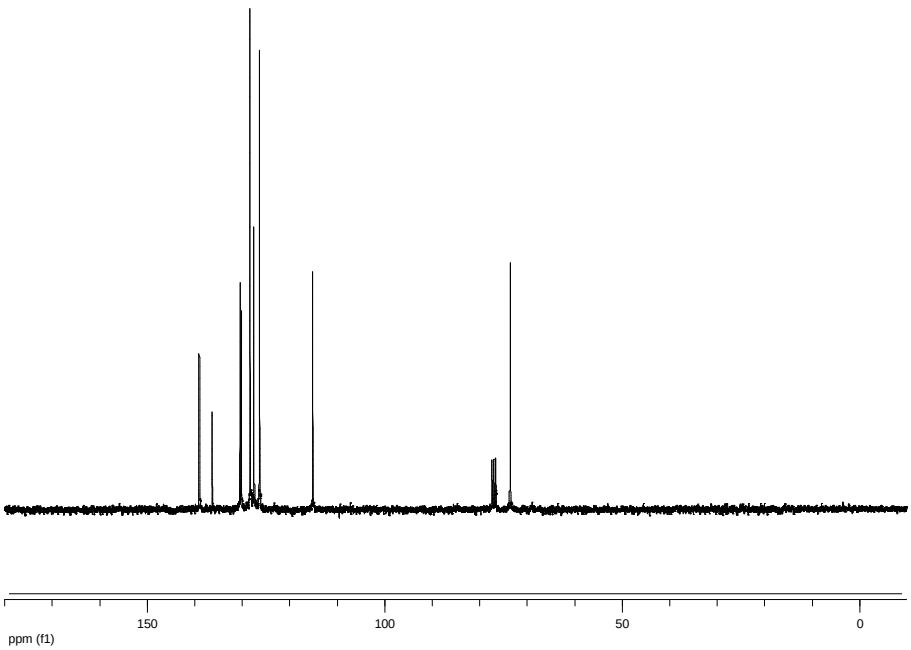
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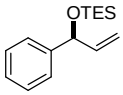
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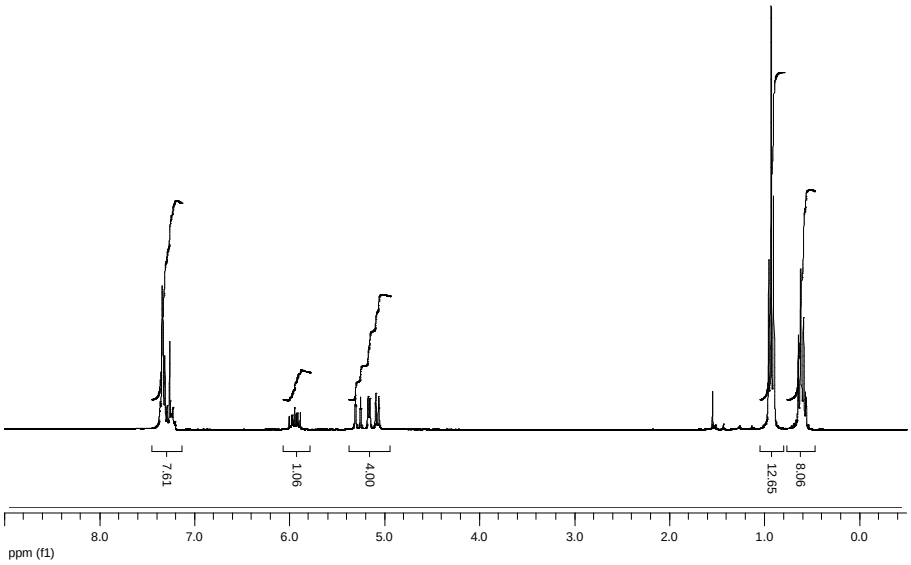
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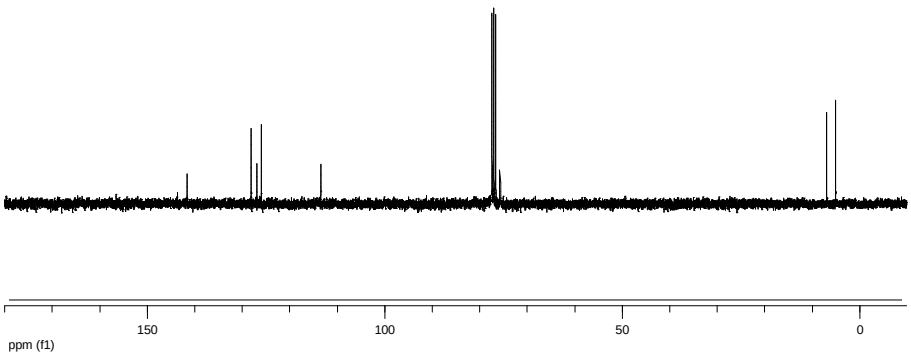
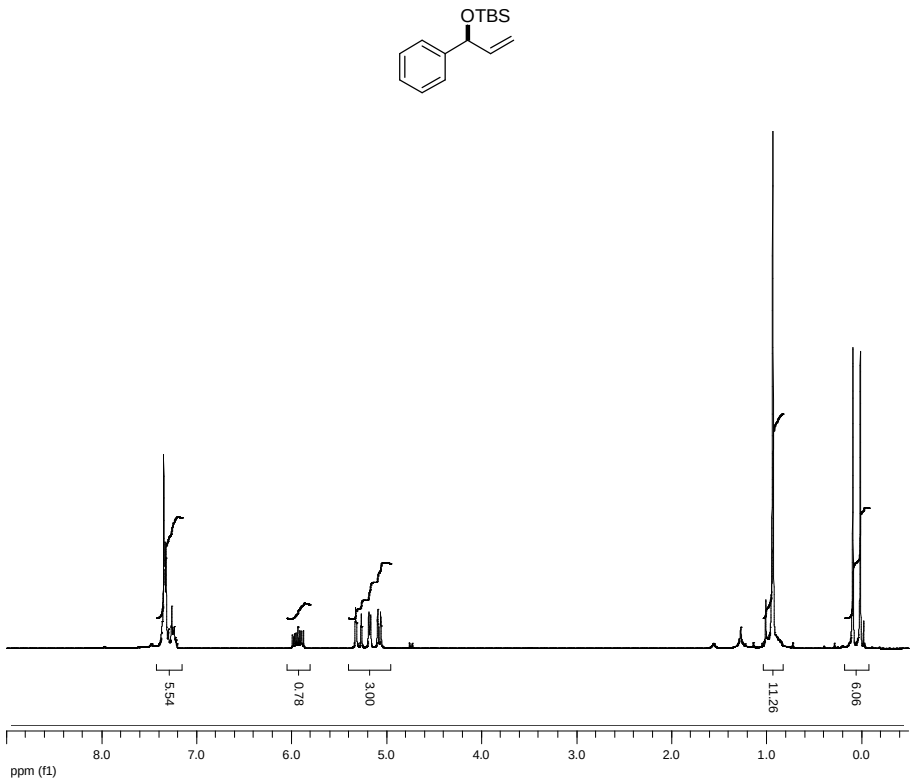
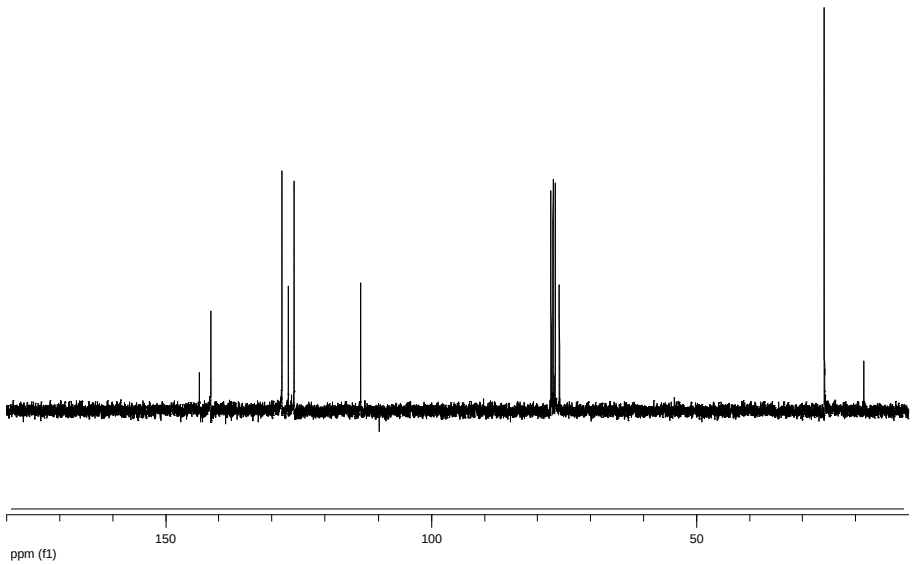
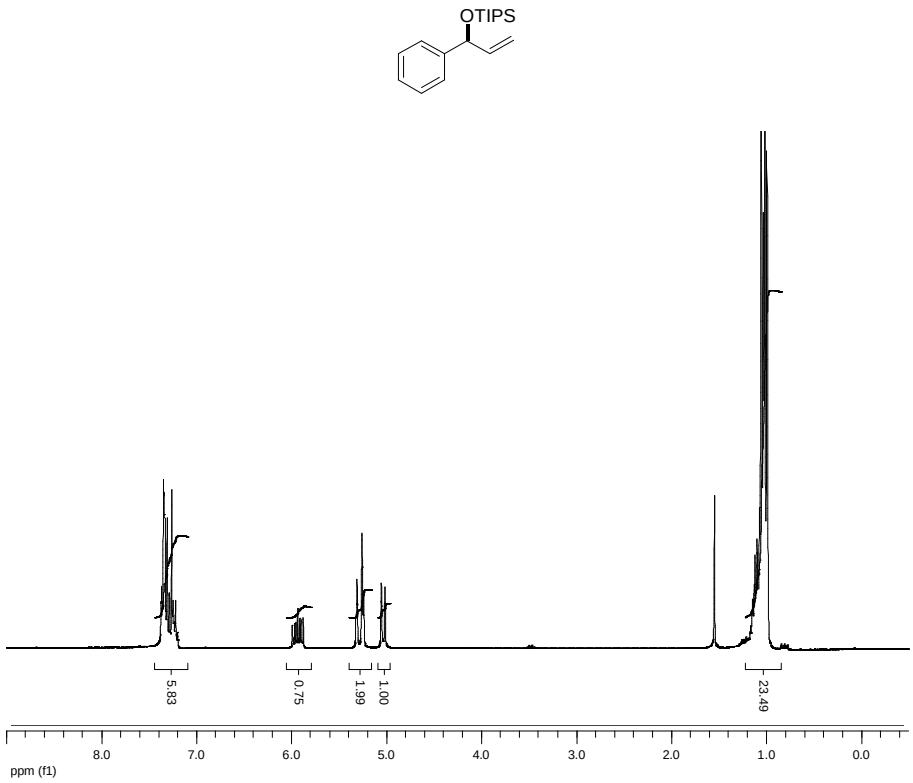
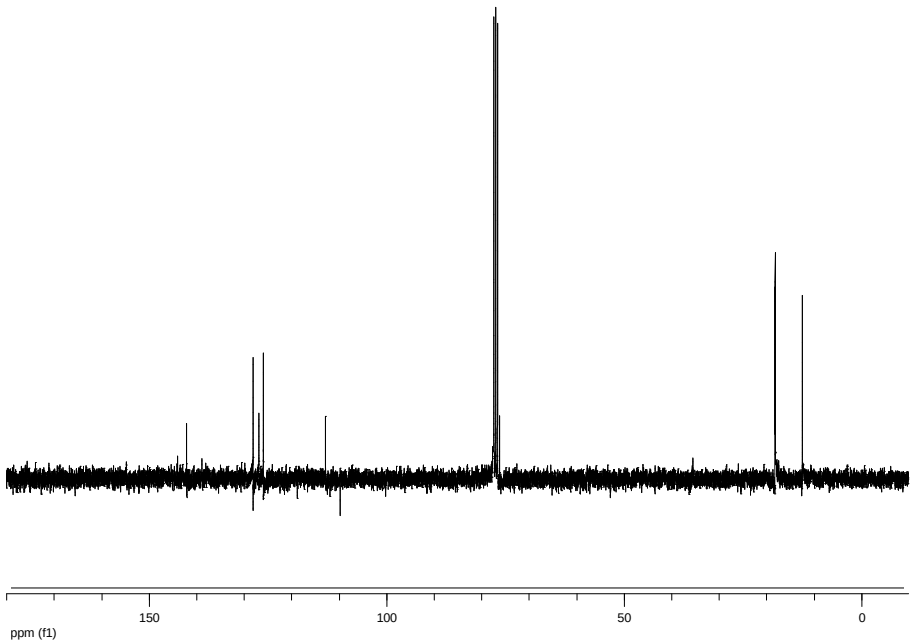
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

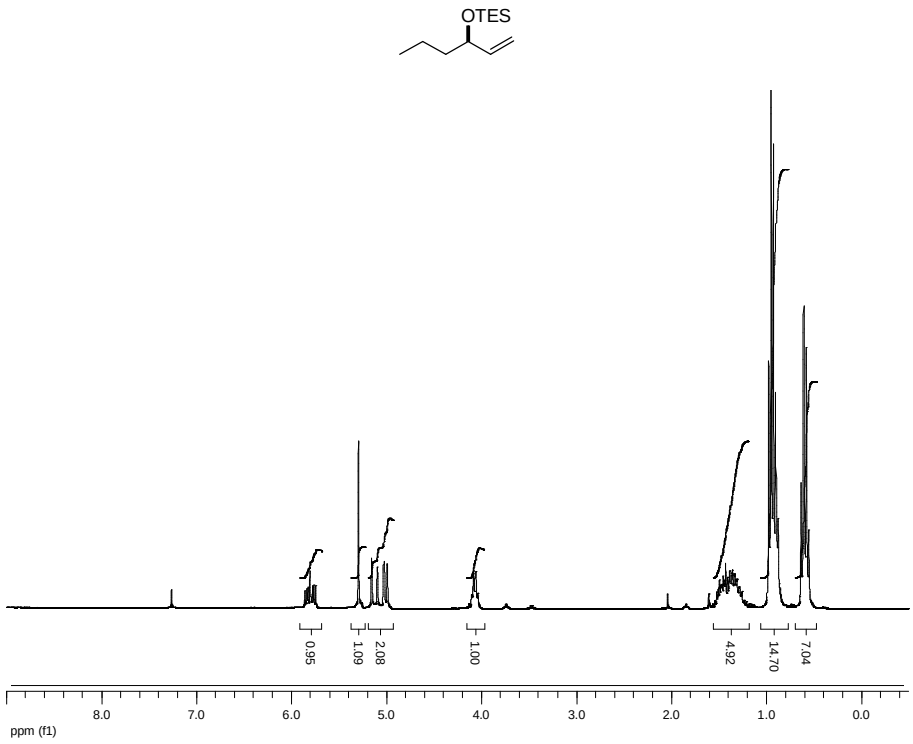

150
100
50
0
ppm (f1)

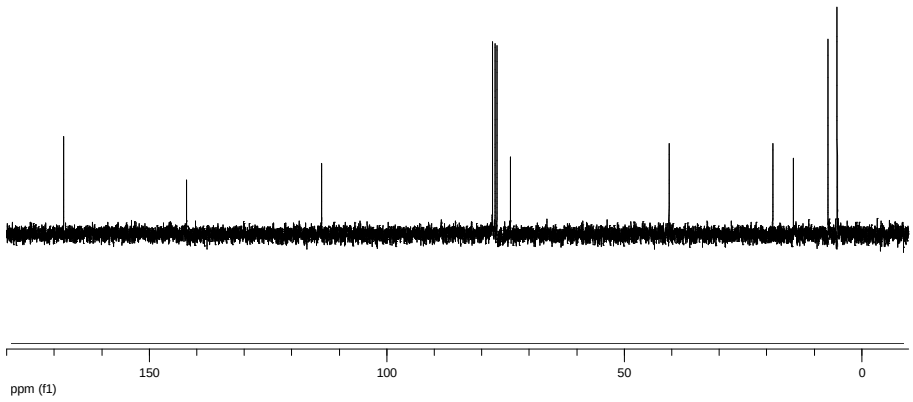

OTBS
5.54
0.78
3.00
11.26
6.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


150
100
50
ppm (f1)


OTIPS
5.83
0.75
1.99
1.00
23.49
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


150
100
50
0
ppm (f1)


OTES
0.95
1.09
2.08
1.00
4.92
14.70
7.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


150
100
50
0
ppm (f1)